

**Stereochemical Models for Rh-Catalyzed
Amination Reactions of Chiral Sulfamates**

Supplementary Material
(11 pages)

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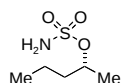
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General. All reagents were obtained commercially unless otherwise noted. Reactions were performed using oven-dried glassware under an atmosphere of dry nitrogen. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated under reduced pressure (ca. 15 mm Hg) by rotary evaporation. Dichloromethane, acetonitrile, and pyridine were freshly distilled from CaH₂ immediately prior to use. Tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME) were freshly distilled from sodium benzophenone ketyl immediately prior to use. *N,N*-Dimethylformamide (DMF) and *N,N*-Dimethylacetamide (DMA) were dried over activated 4Å molecular sieves. Chlorosulfonyl isocyanate was obtained from Acros Chemicals, transferred via cannula to a Schlenk flask, and stored at -20 °C. Light magnesium oxide was flame-dried under reduced pressure (1 mm Hg) prior to use. Chromatographic purification of products was accomplished using forced-flow chromatography on EM Science Geduran silica gel 60 (35–75 µm). Compounds purified by chromatography on silica gel were applied to the adsorbent bed using the indicated solvent conditions with a minimum amount of added chloroform if needed for solubility. Thin layer chromatography was performed on EM Science silica gel 60 F₂₅₄ plates (250 µm). Visualization of the developed chromatogram was accomplished by fluorescence quenching and by staining with ethanolic anisaldehyde, aqueous potassium permanganate, or aqueous ceric ammonium molybdate (CAM) solution.

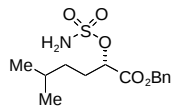
Nuclear magnetic resonance (NMR) spectra were acquired on Varian XL-400 and Varian XL-500 instruments, operating at 400 or 500 and 100 or 125 MHz (as indicated) for ¹H and ¹³C, respectively, and are referenced internally to solvent signals. Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet), integration, coupling constant (Hz). Data for ¹³C are reported in terms of chemical shift (δ, ppm). Infrared spectra were collected on a Thermo Nicolet IR300 spectrometer and are reported in terms of frequency of absorption. Sample preparation was done as a thin film on a NaCl plate. High-resolution mass spectra were obtained from the Mass Spectrometry Facility, University of California at San Francisco, supported by the NIH Division of Research and Resources and from the High Resolution Mass Spectrometry Facility, University of California at Riverside.

For general experimental protocols, see: Espino, C. G.; Wehn, P. M.; Chow, J.; Du Bois, J. *J. Am. Chem. Soc.* **2001**, *123*, 6935-6936.

Characterization data for sulfamate esters from Table 1 and eqs 1–4:

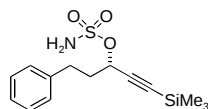


Purified by chromatography on silica gel (4:1 hexanes/EtOAc); colorless oil: TLC *R_f* = 0.27 (4:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 4.91 (br s, 2H), 4.70 (sext, 1H, *J* = 6.4 Hz), 1.77–1.67 (m, 1H), 1.57 (ddt, 1H, *J* = 13.6, 9.8, 5.8 Hz), 1.50–1.35 (m, 2H), 1.41 (d, 3H, *J* = 6.4 Hz), 0.94 (t, 3H, *J* = 7.2 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 81.5, 38.5, 20.5, 18.3, 13.7 ppm; IR (thin film) ν 3368, 3291, 2963, 2875, 1559, 1353, 1180, 924 cm⁻¹; HRMS (EI) calcd for C₅H₁₃NO₃S 167.0616 found 190.0516 (MNa⁺).

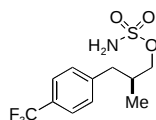


Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid: TLC *R_f* = 0.20 (4:1 hexanes/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 7.42–7.33 (m, 5H), 5.28 (d, 1H, *J* = 12.2 Hz), 5.18 (d, 1H, *J* = 12.0 Hz), 5.12 (br s, 2H), 4.98 (dd, 1H, *J* = 7.4, 4.6 Hz), 1.98–1.82 (m, 2H), 1.59–1.45 (m, 1H), 1.32 (ddt, 1H, *J* = 13.2, 10.6, 6.0 Hz), 1.26–1.16 (m, 1H), 0.86 (d, 3H, *J* = 6.7 Hz), 0.84 (d, 3H, *J* = 6.6 Hz) ppm; ¹³C NMR (CDCl₃, 100 MHz) δ 170.2, 134.7, 128.8, 128.7, 128.4, 79.9, 67.7, 33.3, 29.8, 27.5, 22.4, 22.1 ppm; IR (thin film) ν 3379, 3283, 3036, 2958,

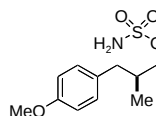
2872, 1744, 1556, 1383, 1290, 1187, 1019, 939, 826, 738 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_5\text{S}$ 315.1140 found 333.1488 (MNH_4^+).



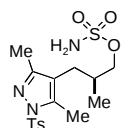
Purified by chromatography on silica gel (17:3 hexanes/EtOAc); colorless oil: TLC R_f = 0.29 (4:1 hexanes/EtOAc); ^1H NMR (CD_3OD , 400 MHz) δ 7.30-7.14 (m, 5H), 5.03 (t, 1H, J = 6.4 Hz), 4.85 (br s, 2H), 2.85-2.71 (m, 2H), 2.20-2.03 (m, 2H), 0.18 (s, 9H) ppm; ^{13}C NMR (CD_3OD , 100 MHz) δ 141.9, 129.5, 129.4, 127.2, 102.7, 93.6, 71.3, 38.6, 31.9, -0.3 ppm; IR (thin film) ν 3387, 3290, 2960, 2179, 1554, 1455, 1376, 1251, 1189, 917, 845, 700 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_3\text{SSi}$ 311.1011 found 231.1218 ($\text{M}^+ - \text{SO}_2\text{NH}_2$).



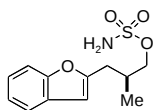
Purified by chromatography on silica gel (2:1 hexanes/EtOAc); colorless oil: TLC R_f = 0.23 (2:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.55 (d, 2H, J = 8.0 Hz), 7.28 (d, 2H, J = 7.9 Hz), 5.02 (br s, 2H), 4.05 (d, 2H, J = 5.8 Hz), 2.85 (dd, 1H, J = 13.6, 6.3 Hz), 2.54 (dd, 1H, J = 13.5, 8.1 Hz), 2.27-2.16 (m, 1H), 0.97 (d, 3H, J = 6.7 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 143.4, 129.4, 128.7 (q, $J_{\text{C-F}}$ = 32 Hz), 125.3, 125.2, 74.7, 38.8, 34.6, 16.1 ppm; IR (thin film) ν 3382, 3277, 1326, 1180, 1118, 1067 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{14}\text{F}_3\text{NO}_3\text{S}$ 297.0646 found 278.0664 ($\text{M}^+ - \text{F}$).



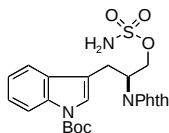
Purified by chromatography on silica gel (2:1 hexanes/EtOAc); colorless oil: TLC R_f = 0.22 (2:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.07 (d, 2H, J = 8.6 Hz), 6.83 (d, 2H, J = 8.6 Hz), 5.12 (br s, 2H), 4.04 (dd, 1H, J = 9.3, 5.7 Hz), 4.00 (dd, 1H, J = 9.3, 6.0 Hz), 3.78 (s, 3H), 2.69 (dd, 1H, J = 13.7, 6.6 Hz), 2.44 (dd, 1H, J = 13.7, 7.8 Hz), 2.18-2.08 (m, 1H), 0.96 (d, 3H, J = 6.8 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 157.9, 131.2, 130.0, 113.7, 74.9, 55.2, 38.0, 34.7, 16.2 ppm; IR (thin film) ν 3379, 3287, 1636, 1512, 1362, 1245, 1178, 975, 803 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{17}\text{NO}_4\text{S}$ 259.0878 found 259.0868 (M^+).



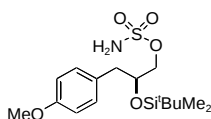
Purified by chromatography on silica gel (1:1 hexanes/EtOAc); white foam: TLC R_f = 0.26 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.77 (d, 2H, J = 8.4 Hz), 7.30 (d, 2H, J = 8.4 Hz), 5.44 (br s, 2H), 3.97 (d, 2H, J = 5.6 Hz), 2.44 (dd, 1H, J = 14.8, 6.4 Hz), 2.40 (s, 3H), 2.39 (s, 3H), 2.16 (s, 3H), 2.16-2.10 (m, 1H), 2.01-1.89 (m, 1H), 0.88 (d, 3H, J = 7.2 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.5, 145.3, 140.7, 135.0, 129.9, 127.4, 119.4, 74.3, 33.6, 26.5, 21.6, 16.1, 12.4, 11.4 ppm; IR (thin film) ν 3367, 3292, 3088, 2968, 2932, 1595, 1369, 1296, 1175, 1093, 977, 931, 815, 670 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{23}\text{N}_3\text{O}_5\text{S}_2$ 401.1079 found 402.1145 (MH^+).



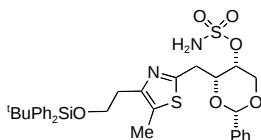
Purified by chromatography on silica gel (CH_2Cl_2); white solid: TLC R_f = 0.29 (CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ 7.50 (dd, 1H, J = 6.9, 2.2 Hz), 7.42 (d, 1H, J = 8.0 Hz), 7.23 (td, 1H, J = 7.2, 1.6 Hz), 7.20 (td, 1H, J = 7.2, 1.3 Hz), 6.46 (s, 1H), 5.02 (br s, 2H), 4.15-4.08 (m, 2H), 2.92 (dd, 1H, J = 15.0, 6.4 Hz), 2.73 (dd, 1H, J = 14.9, 7.4 Hz), 2.48-2.36 (m, 1H), 1.07 (d, 3H, J = 6.9 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 156.2, 154.7, 128.6, 123.4, 122.6, 120.4, 110.8, 103.9, 74.6, 32.1, 31.6, 16.3 ppm; IR (thin film) ν 3384, 3284, 2967, 1555, 1451, 1365, 1247, 1179, 975, 939, 749 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_4\text{S}$ 269.0722 found 269.0728 (M^+).



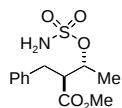
Purified by chromatography on silica gel (6:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$); pale yellow solid: TLC R_f = 0.41 (5:1 $\text{CH}_2\text{Cl}_2/\text{EtOAc}$); ^1H NMR (CDCl_3 , 400 MHz) δ 8.11-8.01 (m, 1H), 7.76 (dd, 2H, J = 5.3, 3.1 Hz), 7.66 (dd, 2H, J = 5.5, 3.0 Hz), 7.55 (d, 1H, J = 7.6 Hz), 7.42 (s, 1H), 7.28 (t, 1H, J = 7.8 Hz), 7.20 (t, 1H, J = 7.6 Hz), 5.14 (br s, 2H), 5.07-4.98 (m, 1H), 4.87 (t, 1H, J = 10.1 Hz), 4.48 (dd, 1H, J = 10.6, 4.5 Hz), 3.38 (dd, 1H, J = 14.9, 8.4 Hz), 3.28 (dd, 1H, J = 15.0, 7.1 Hz), 1.61 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 168.3, 149.5, 135.4, 134.2, 131.4, 129.8, 124.6, 123.9, 123.4, 122.7, 118.7, 115.3, 115.2, 83.8, 68.9, 49.9, 28.1, 24.6 ppm; IR (thin film) ν 3366, 3275, 2975, 1709, 1451, 1369, 1256, 1184, 1089, 994, 717 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{25}\text{N}_3\text{O}_7\text{S}$ 499.1413 found 302.1058 ($\text{M}^+ - \text{CO}_2^t\text{Bu} - \text{OSO}_2\text{NH}_2$).



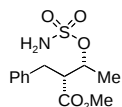
Purified by chromatography on silica gel (3:1 hexanes/ EtOAc); colorless oil: TLC R_f = 0.23 (3:1 hexanes/ EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.14 (d, 2H, J = 8.5 Hz), 6.86 (d, 2H, J = 8.5 Hz), 5.24 (s, 2H), 4.17-4.03 (m, 3H), 3.80 (s, 3H), 2.87 (dd, 1H, J = 13.8, 5.8 Hz), 2.74 (dd, 1H, J = 13.8, 6.5 Hz), 0.90 (s, 9H), 0.06 (s, 3H), -0.10 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 158.4, 129.3, 128.4, 113.9, 73.5, 71.8, 55.3, 39.6, 25.8, 18.1, -4.8, -5.1 ppm; IR (thin film) ν 3375, 3284, 2954, 2857, 1613, 1513, 1367, 1249, 1182, 1118, 991, 835, 738 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{29}\text{NO}_5\text{SSi}$ 375.1536 found 318.0838 ($\text{M}^+ - \text{C}_4\text{H}_9$).



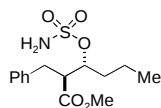
Purified by chromatography on silica gel (1:1 hexanes/ EtOAc); colorless oil: TLC R_f = 0.31 (2:3 hexanes/ EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.67-7.61 (m, 4H), 7.54-7.32 (m, 11H), 6.60 (s, 2H), 5.53 (s, 1H), 4.53-4.46 (m, 2H), 4.23-4.15 (m, 1H), 3.98 (d, 1H, J = 11.9 Hz), 3.87-3.77 (m, 2H), 3.49 (dd, 1H, J = 14.5, 8.7 Hz), 3.32 (dd, 1H, J = 14.4, 5.5 Hz), 2.93 (t, 2H, J = 6.3 Hz), 2.22 (s, 3H), 1.08 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.5, 147.9, 137.1, 135.4, 133.2, 129.7, 129.1, 129.0, 128.2, 127.7, 126.1, 101.2, 77.6, 73.2, 69.8, 63.7, 34.2, 29.5, 26.7, 19.1, 14.4 ppm; IR (thin film) ν 3301, 3184, 3070, 2931, 2858, 1559, 1383, 1182, 1111, 908, 823, 701 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{33}\text{H}_{40}\text{N}_2\text{O}_6\text{S}_2\text{Si}$ 652.2097 found 653.2149 (MH^+).



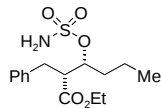
Purified by chromatography on silica gel (7:3 hexanes/EtOAc); clear oil: TLC R_f = 0.23 (7:3 hexanes/EtOAc); ^1H NMR (CDCl_3 , 500 MHz) δ 7.28 (t, 2H, J = 7.8 Hz), 7.21 (t, 1H, J = 7.5 Hz), 7.16 (d, 2H, J = 7.0 Hz), 5.07 (br s, 2H), 4.94-4.88 (m, 1H), 3.58 (s, 3H), 3.07-2.95 (m, 3H), 1.50 (d, 3H, J = 6.5 Hz) ppm; ^{13}C NMR (CDCl_3 , 125 MHz) δ 172.7, 138.1, 128.7, 128.6, 126.7, 79.7, 53.0, 52.0, 34.1, 18.7 ppm; IR (thin film) ν 3368, 3274, 3030, 2953, 1724, 1367, 1183, 701 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{17}\text{NO}_5\text{S}$ 287.0827 found 305.1161 (MNH_4^+).



Purified by chromatography on silica gel (7:3 hexanes/EtOAc); colorless oil: TLC R_f = 0.27 (7:3 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.31-7.26 (m, 2H), 7.24-7.19 (m, 1H), 7.17-7.13 (m, 2H), 5.07 (br s, 2H), 4.91 (dq, 1H, J = 7.2, 6.4 Hz), 3.55 (s, 3H), 3.02 (ddd, 1H, J = 9.0, 7.3, 6.0 Hz), 2.95-2.89 (m, 2H), 1.53 (d, 3H, J = 6.4 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.9, 137.7, 128.8, 128.5, 126.8, 79.8, 53.2, 52.0, 33.9, 18.5 ppm; IR (thin film) ν 3368, 3273, 2953, 1725, 1372, 1184, 923, 701 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{17}\text{NO}_5\text{S}$ 287.0827 found 310.0734 (MNa^+).

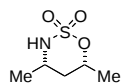


Purified by chromatography on silica gel (4:1 hexanes/EtOAc); colorless oil: TLC R_f = 0.22 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.31-7.15 (m, 5H), 5.41 (s, 2H), 4.86 (dt, 1H, J = 7.6, 4.7 Hz), 3.59 (s, 3H), 3.16-3.00 (m, 2H), 2.95 (dd, 1H, J = 13.6, 4.5 Hz), 1.87-1.68 (m, 2H), 1.60-1.36 (m, 2H), 0.95 (t, 3H, J = 7.3 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 173.4, 138.4, 128.8, 128.6, 126.7, 83.4, 52.2, 51.0, 34.3, 33.2, 18.4, 13.8 ppm; IR (thin film) ν 3372, 3278, 3029, 2962, 2875, 1726, 1560, 1370, 1184, 923, 701 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_5\text{S}$ 315.1140 found 333.1475 (MNH_4^+).



Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid: mp 145–147 $^{\circ}\text{C}$; TLC R_f = 0.17 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.29-7.24 (m, 2H), 7.23-7.16 (m, 3H), 5.12 (s, 2H), 4.87 (q, 1H, J = 5.8 Hz), 4.06-3.98 (m, 2H), 3.19 (dt, 1H, J = 8.0, 6.8 Hz), 2.93 (d, 2H, J = 7.2 Hz), 1.83-1.76 (m, 2H), 1.54-1.44 (m, 2H), 1.07 (t, 3H, J = 7.2 Hz), 0.96 (t, 3H, J = 7.4 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 172.5, 138.2, 128.9, 128.4, 126.6, 83.5, 61.0, 51.0, 33.5, 33.4, 17.7, 13.9, 13.8 ppm; IR (thin film) ν 3368, 3275, 3088, 2964, 2936, 1721, 1560, 1455, 1377, 1184, 1032, 923, 701 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{23}\text{NO}_5\text{S}$ 329.1297 found 347.1629 (MNH_4^+).

Characterization data for oxathiazinane products from Table 1 and eqs 1–4:

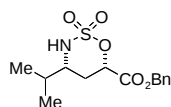
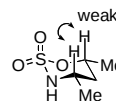


Purified by chromatography on silica gel (1:9 hexanes/ CH_2Cl_2); colorless oil (3:1 ds, 88%). **syn isomer:** white solid, mp 64–66 $^{\circ}\text{C}$; TLC R_f = 0.30 (1:9 hexanes/ CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ 5.26 (dq, 1H, J = 11.6,

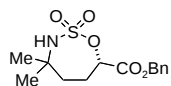
6.4, 2.2 Hz), 3.94 (br d, 1H, $J = 10.0$ Hz), 3.83-3.71 (m, 1H), 1.80 (dt, 1H, $J = 14.4, 2.4$ Hz), 1.43-1.33 (m, 1H), 1.41 (d, 3H, $J = 6.8$ Hz), 1.26 (d, 3H, $J = 6.8$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 80.7, 51.1, 39.0, 21.1, 20.8 ppm; IR (thin film) ν 3260, 2983, 2939, 1421, 1357, 1187, 1092, 934, 860, 793 cm^{-1} ; HRMS (EI) calcd for $\text{C}_5\text{H}_{11}\text{NO}_3\text{S}$ 165.0460 found 188.0354 (MNa^+). **anti isomer:** TLC $R_f = 0.24$ (1:9 hexanes/ CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ 5.04 (dq, 1H, $J = 8.8, 6.4, 3.6$ Hz), 4.41 (br d, 1H, $J = 6.4$ Hz), 3.90-3.78 (m, 1H), 1.84 (ddd, 1H, $J = 14.6, 8.6, 4.8$ Hz), 1.68 (ddd, 1H, $J = 14.6, 4.8, 3.6$ Hz), 1.50 (d, 3H, $J = 6.4$ Hz), 1.45 (d, 1H, $J = 7.2$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 78.7, 49.2, 35.8, 20.7, 19.6 ppm; IR (thin film) ν 3268, 2984, 2941, 1422, 1364, 1183, 1087, 876, 797 cm^{-1} .

^1H NMR (CDCl_3 , 600 MHz) NOESY correlations for major (*syn*) diastereomer:

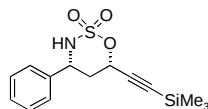
No observed nOe for minor (*anti*) diastereomer



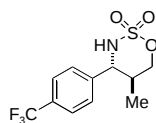
Purified by chromatography on silica gel (3:6:1 hexanes/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$); oily solid (8:1 ds, 55%): TLC $R_f = 0.53$ (3:6:1 hexanes/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$); ^1H NMR (CDCl_3 , 400 MHz) δ 7.42-7.33 (m, 5H), 5.26 (d, 1H, $J = 12.0$ Hz), 5.22 (d, 1H, $J = 12.0$ Hz), 5.19 (dd, 1H, $J = 12.4, 2.4$ Hz), 4.32 (br d, 1H, $J = 11.2$ Hz), 3.50 (dddd, 1H, $J = 12.0, 10.8, 6.6, 2.6$ Hz), 2.11 (dt, 1H, $J = 14.2, 2.6$ Hz), 1.84-1.71 (m, 2H), 1.01 (d, 3H, $J = 6.8$ Hz), 0.99 (d, 3H, $J = 6.7$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.1, 134.4, 128.8, 128.7, 128.6, 78.7, 68.0, 60.5, 32.3, 29.4, 18.5, 18.1 ppm; IR (thin film) ν 3257, 2967, 2879, 1750, 1425, 1366, 1193, 1072, 884, 750 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_5\text{S}$ 313.0984 found 331.1327 (MNH_4^+).



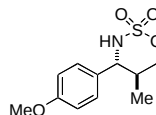
Purified by chromatography on silica gel (3:6:1 hexanes/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$); colorless oil (25%): TLC $R_f = 0.40$ (3:6:1 hexanes/ $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$); ^1H NMR (CDCl_3 , 400 MHz) δ 7.40-7.33 (m, 5H), 5.23 (d, 1H, $J = 12.2$ Hz), 5.20 (d, 1H, $J = 12.2$ Hz), 5.06 (br s, 1H), 4.88-4.83 (m, 1H), 2.35-2.19 (m, 3H), 1.91 (ddd, 1H, $J = 14.4, 6.0, 2.8$ Hz), 1.34 (s, 3H), 1.29 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 168.0, 134.8, 128.7/(2), 128.4, 78.9, 67.7, 54.6, 39.4, 30.6, 28.1, 27.8 ppm; IR (thin film) ν 3294, 2975, 1746, 1428, 1356, 1181, 1028, 915 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_5\text{S}$ 313.0984 found 331.1341 (MNH_4^+).



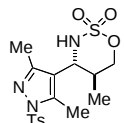
Purified by chromatography on silica gel (1:1 hexanes/ CH_2Cl_2); off-white solid (20:1 ds, 62%): TLC $R_f = 0.44$ (3:7 hexanes/ CH_2Cl_2); ^1H NMR (C_6D_6 , 500 MHz) δ 7.02-6.94 (m, 3H), 6.61-6.57 (m, 2H), 5.17 (dd, 1H, $J = 11.8, 2.3$ Hz), 4.28 (td, 1H, $J = 11.1, 2.3$ Hz), 3.65 (br d, 1H, $J = 10.0$ Hz), 1.67-1.57 (m, 1H), 1.36 (dt, 1H, $J = 14.0, 2.5$ Hz), 0.14 (s, 9H) ppm; ^{13}C NMR (C_6D_6 , 100 MHz) δ 137.7, 128.8, 128.6, 126.5, 99.8, 93.8, 72.8, 57.6, 36.3, -0.5 ppm; IR (thin film) ν 3263, 2961, 1415, 1366, 1191, 1094, 1011, 840, 698 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_3\text{SSi}$ 309.0855 found 332.0767 (MNa^+).



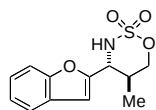
Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (20:1 ds, 70%): TLC R_f = 0.47 (2:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.69 (d, 2H, J = 8.2 Hz), 7.47 (d, 2H, J = 7.9 Hz), 4.58 (br d, 1H, J = 8.5 Hz), 4.55-4.47 (m, 2H), 4.43 (dd, 1H, J = 10.8, 8.5 Hz), 2.45-2.32 (m, 1H), 0.72 (d, 3H, J = 6.7 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 151.0, 140.7, 131.4 (q, $J_{\text{C-F}}$ = 32 Hz), 127.8, 126.3, 76.5, 65.0, 33.9, 11.8 ppm; IR (thin film) ν 3266, 1433, 1360, 1324, 1188, 1120, 1070, 971 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{12}\text{F}_3\text{NO}_3\text{S}$ 295.0490 found 276.0506 ($\text{M}^+ - \text{F}$).



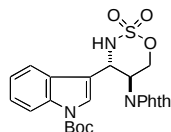
Purified by chromatography on silica gel (3:1 hexanes/EtOAc); white solid (20:1 ds, 85%): TLC R_f = 0.30 (2:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.23 (d, 2H, J = 8.8 Hz), 6.92 (d, 2H, J = 8.6 Hz), 4.50-4.42 (m, 3H), 4.29 (dd, 1H, J = 10.8, 8.6 Hz), 3.81 (s, 3H), 2.39-2.26 (m, 1H), 0.70 (d, 3H, J = 6.8 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.0, 129.2, 128.4, 114.6, 76.5, 64.9, 55.3, 34.0, 11.9 ppm; IR (thin film) ν 3266, 2940, 1614, 1514, 1419, 1356, 1252, 1184, 1025, 971 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{11}\text{H}_{15}\text{NO}_4\text{S}$ 257.0722 found 257.0717 (M^+).



Purified by chromatography on silica gel (13:7 hexanes/EtOAc); white foam (20:1 ds, 84%): TLC R_f = 0.48 (1:3 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.82 (d, 2H, J = 8.4 Hz), 7.32 (d, 2H, J = 8.0 Hz), 4.52 (br d, 1H, J = 6.8 Hz), 4.44 (dd, 1H, J = 11.6, 5.6 Hz), 4.39 (t, 1H, J = 11.2 Hz), 4.28 (dd, 1H, J = 11.4, 6.6 Hz), 2.54 (s, 3H), 2.47-2.35 (m, 1H), 2.42 (s, 3H), 2.27 (s, 3H), 0.68 (d, 3H, J = 6.8 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 151.1, 145.8, 142.2, 134.6, 130.1, 127.7, 116.8, 76.5, 56.8, 32.5, 21.7, 13.7, 11.7, 11.5 ppm; IR (thin film) ν 3268, 2971, 2934, 2883, 1595, 1424, 1367, 1177, 1096, 972, 732, 670 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{21}\text{N}_3\text{O}_5\text{S}_2$ 399.0923 found 400.1018 (MH^+).

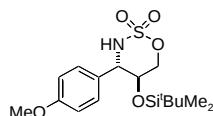


Purified by chromatography on silica gel (1:3 hexanes/ CH_2Cl_2); white solid (20:1 ds, 65%): TLC R_f = 0.35 (1:3 hexanes/ CH_2Cl_2); ^1H NMR (CDCl_3 , 400 MHz) δ 7.58 (d, 1H, J = 7.8 Hz), 7.48 (d, 1H, J = 8.2 Hz), 7.33 (td, 1H, J = 7.4, 1.4 Hz), 7.26 (td, 1H, J = 7.4, 1.4 Hz), 6.75 (s, 1H), 4.92 (br d, 1H, J = 10.4 Hz), 4.65 (t, 1H, J = 10.7 Hz), 4.49 (d, 2H, J = 8.3 Hz), 2.61-2.48 (m, 1H), 0.82 (d, 3H, J = 6.8 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 154.7, 151.2, 127.3, 125.0, 123.3, 121.5, 111.3, 106.0, 76.0, 59.2, 32.1, 11.9 ppm; IR (thin film) ν 3259, 2969, 1614, 1421, 1371, 1191, 1089, 969, 914, 790 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_4\text{S}$ 267.0565 found 267.0568 (M^+).

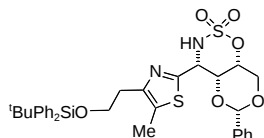


Purified by chromatography on silica gel (30:1 CH_2Cl_2 /EtOAc); white solid (12:1 ds, 85%): TLC R_f = 0.50 (20:1 CH_2Cl_2 /EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 8.07-7.99 (m, 1H), 7.78 (dd, 2H, J = 5.4, 3.1 Hz), 7.74-7.68 (m,

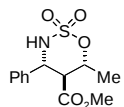
4H), 7.32-7.22 (m, 2H), 6.16 (t, 1H, $J = 10.5$ Hz), 5.43 (t, 1H, $J = 11.2$ Hz), 5.15 (td, 1H, $J = 11.2, 4.8$ Hz), 5.00 (br d, 1H, $J = 9.8$ Hz), 4.50 (dd, 1H, $J = 11.0, 4.7$ Hz), 1.68 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.3, 149.1, 135.2, 134.6, 131.0, 128.1, 125.3, 124.1, 123.8, 123.1, 119.1, 115.1, 114.9, 84.6, 69.0, 51.2, 46.9, 27.9 ppm; IR (thin film) ν 3259, 2976, 1714, 1453, 1382, 1273, 1193, 1152, 1075, 1021, 971 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}_7\text{S}$ 497.1257 found 300.0881 ($\text{M}^+ - \text{CO}_2^t\text{Bu} - \text{OSO}_2\text{NH}_2$).



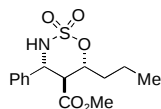
Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (10:1 ds, 77%): mp 133–135 °C; TLC $R_f = 0.28$ (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.23 (d, 2H, $J = 8.7$ Hz), 6.90 (d, 2H, $J = 8.7$ Hz), 4.89 (d, 1H, $J = 8.2$ Hz), 4.52-4.43 (m, 2H), 4.32 (dd, 1H, $J = 11.2, 5.2$ Hz), 3.98 (td, 1H, $J = 9.9, 5.2$ Hz), 3.80 (s, 3H), 0.70 (s, 9H), -0.13 (s, 3H), -0.56 (s, 3H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.1, 128.9, 128.5, 114.3, 73.5, 67.4, 63.9, 55.4, 25.4, 17.7, -5.0, -5.8 ppm; IR (thin film) ν 3281, 2955, 2931, 2857, 1614, 1518, 1368, 1253, 1193, 1035, 839, 779 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{27}\text{NO}_5\text{Si}$ 373.1379 found 316.0676 ($\text{M}^+ - \text{C}_4\text{H}_9$).



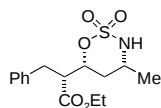
Purified by chromatography on silica gel (1:1 hexanes/EtOAc); white solid (20:1 ds, 92%): TLC $R_f = 0.37$ (2:3 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.64-7.57 (m, 4H), 7.48-7.25 (m, 11H), 5.66 (s, 1H), 4.64 (s, 1H), 4.47-4.38 (m, 2H), 4.17 (d, 1H, $J = 12.5$ Hz), 3.90-3.78 (m, 3H), 3.41 (dd, 1H, $J = 14.3, 5.5$ Hz), 3.03-2.86 (m, 2H), 2.51 (s, 3H), 1.04 (s, 9H) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 163.0, 144.6, 137.2, 135.3, 132.5, 132.3, 129.9, 128.9, 128.7, 128.2, 128.0, 127.9, 127.8, 126.1, 101.8, 75.8, 71.1, 70.6, 62.3, 32.8, 30.3, 26.7, 18.9, 12.2 ppm; IR (thin film) ν 3070, 2931, 2858, 2251, 1589, 1428, 1314, 1159, 1083, 912, 735, 702 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{33}\text{H}_{38}\text{N}_2\text{O}_6\text{S}_2\text{Si}$ 650.1941 found 593.1226 ($\text{M}^+ - \text{C}_4\text{H}_9$).



Purified by chromatography on silica gel (4:1 hexanes/EtOAc); white solid (20:1 ds, 87%): TLC $R_f = 0.26$ (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.40-7.15 (m, 5H), 5.06 (qd, 1H, $J = 6.1, 4.4$ Hz), 4.95-4.82 (m, 2H), 3.45 (s, 3H), 2.92 (t, 1H, $J = 10.6$ Hz), 1.42 (d, 3H, $J = 6.0$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 169.5, 135.4, 129.4, 129.2, 127.0, 80.8, 61.2, 53.7, 52.4, 19.5 ppm; IR (thin film) ν 3266, 3036, 2955, 1732, 1433, 1373, 1310, 1193, 1067, 910, 809, 733 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{12}\text{H}_{15}\text{NO}_5\text{S}$ 285.0671 found 303.1006 (MNH_4^+).

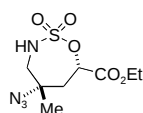


Purified by chromatography on silica gel (17:3 hexanes/EtOAc); white solid (20:1 ds, 66%): mp 148–150 °C; TLC $R_f = 0.55$ (7:3 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.43-7.25 (m, 5H), 5.12-4.89 (m, 2H), 4.65 (d, 1H, $J = 9.4$ Hz), 3.46 (s, 3H), 2.96 (t, 1H, $J = 10.8$ Hz), 1.80-1.42 (m, 4H), 0.94 (t, 3H, $J = 6.9$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 169.5, 135.5, 129.5, 129.3, 127.0, 84.1, 61.3, 52.6, 52.4, 35.5, 17.6, 13.5 ppm; IR (thin film) ν 3265, 2962, 2876, 1732, 1434, 1373, 1193, 946, 881, 700 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{19}\text{NO}_5\text{S}$ 313.0984 found 313.0986 (M^+).



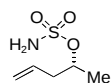
Purified by chromatography on silica gel (3:1 hexanes/EtOAc); white solid (3:1 ds, 84%): mp 152–154 °C; TLC R_f = 0.27 (7:3 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 7.29 (tt, 2H, J = 7.2, 1.7 Hz), 7.25–7.16 (m, 3H), 4.97–4.91 (m, 1H), 4.20 (br d, 1H, J = 10.4 Hz), 4.10 (dq, 1H, J = 10.6, 7.2 Hz), 4.04 (dq, 1H, J = 10.6, 7.2 Hz), 3.83–3.71 (m, 1H), 3.01–2.92 (m, 3H), 1.85 (dt, 1H, J = 14.3, 2.5 Hz), 1.59 (dt, 1H, J = 14.3, 12.0 Hz), 1.28 (d, 3H, J = 6.8 Hz), 1.12 (t, 3H, J = 7.2 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 170.9, 137.4, 129.0, 128.6, 126.8, 82.9, 61.1, 52.2, 51.0, 34.6, 33.4, 20.8, 14.0 ppm; IR (thin film) ν 3259, 2976, 1723, 1421, 1359, 1190, 1025, 865, 702 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{21}\text{NO}_5\text{S}$ 327.1140 found 345.1493 (MNH_4^+).

Characterization data for seven-membered sulfamidate from Figure 3:

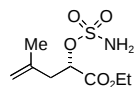


Purified by chromatography on silica gel (3:6:1 hexanes/ CH_2Cl_2 /Et₂O); clear oil (72%): TLC R_f = 0.26 (3:6:1 hexanes/ CH_2Cl_2 /Et₂O); ^1H NMR (CDCl_3 , 400 MHz) δ 5.54 (t, 1H, J = 7.0 Hz), 4.95 (t, 1H, J = 5.6 Hz), 4.31 (dq, 1H, J = 10.8, 7.2 Hz), 4.28 (dq, 1H, J = 10.8, 7.2 Hz), 3.28 (dd, 1H, J = 15.6, 6.4 Hz), 3.20 (dd, 1H, J = 15.2, 7.6 Hz), 2.51 (d, 2H, J = 5.6 Hz), 1.48 (s, 3H), 1.33 (t, 3H, J = 7.2 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.6, 74.6, 62.8, 62.5, 50.3, 41.4, 22.2, 14.0 ppm; IR (thin film) ν 3305, 2983, 2943, 2111, 1744, 1368, 1257, 1185, 1092, 1026, 839 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{14}\text{N}_4\text{O}_5\text{S}$ 278.0685 found 301.0576 (MNa^+).

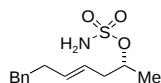
Characterization data for sulfamate esters from Table 2:



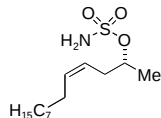
Purified by chromatography on silica gel (3:1 hexanes/EtOAc); colorless oil: TLC R_f = 0.30 (7:3 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 5.79 (ddt, 1H, J = 16.4, 10.8, 7.2 Hz), 5.18–5.15 (m, 1H), 5.13 (t, 1H, J = 1.2 Hz), 4.98 (br s, 2H), 4.73 (sext, 1H, J = 6.2 Hz), 2.48 (dddt, 1H, J = 14.4, 7.2, 6.0, 1.2 Hz), 2.41 (dddt, 1H, J = 14.4, 7.2, 6.0, 1.2 Hz), 1.41 (d, 3H, J = 6.4 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 132.5, 118.9, 80.3, 40.7, 20.1 ppm; IR (thin film) ν 3378, 3289, 3082, 2982, 2938, 1644, 1558, 1359, 1181, 918 cm^{-1} ; HRMS (EI) calcd for $\text{C}_5\text{H}_{11}\text{NO}_3\text{S}$ 165.0460 found 183.0800 (MNH_4^+).



Purified by chromatography on silica gel (97:3 CH_2Cl_2 /EtOAc); colorless oil: TLC R_f = 0.22 (97:3 CH_2Cl_2 /EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 5.49 (br s, 2H), 5.01 (t, 1H, J = 6.5 Hz), 4.87 (s, 1H), 4.81 (s, 1H), 4.22 (q, 2H, J = 7.1 Hz), 2.57 (d, 2H, J = 6.7 Hz), 1.76 (s, 3H), 1.27 (t, 3H, J = 7.1 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 169.9, 138.9, 115.0, 77.5, 62.2, 40.0, 22.1, 14.0 ppm; IR (thin film) ν 3374, 3280, 3082, 2984, 1741, 1654, 1560, 1376, 1186, 1054, 929, 781 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{15}\text{NO}_3\text{S}$ 237.0671 found 237.0676 (M^+).

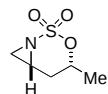


Purified by chromatography on silica gel (3:1 hexanes/EtOAc); colorless oil: TLC R_f = 0.14 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 500 MHz) δ 7.31-7.26 (m, 2H), 7.21-7.16 (m, 3H), 5.57 (dtt, 1H, J = 15.4, 6.5, 1.2 Hz), 5.37 (dtt, 1H, J = 15.0, 6.3, 1.3 Hz), 4.62 (sext, 1H, J = 6.3 Hz), 4.58 (br s, 2H), 2.69 (t, 2H, J = 7.5 Hz), 2.44-2.38 (m, 4H), 1.34 (d, 3H, J = 6.5 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 141.7, 133.9, 128.5, 128.3, 125.8, 124.6, 80.8, 39.5, 35.5, 34.2, 20.1 ppm; IR (thin film) ν 3389, 3285, 3026, 2933, 2854, 1555, 1358, 1183, 927, 699 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{19}\text{NO}_3\text{S}$ 269.1086 found 270.1157 (MH^+).



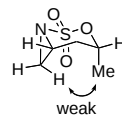
Purified by chromatography on silica gel (17:3 hexanes/EtOAc); colorless oil: TLC R_f = 0.29 (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 5.56 (dtt, 1H, J = 10.8, 7.6, 1.5 Hz), 5.36 (dtt, 1H, J = 10.8, 7.3, 1.5 Hz), 4.77 (br s, 2H), 4.70 (sext, 1H, J = 6.4 Hz), 2.56-2.47 (m, 1H), 2.43-2.34 (m, 1H), 2.03 (q, 2H, J = 6.9 Hz), 1.41 (d, 3H, J = 6.4 Hz), 1.39-1.20 (m, 12H), 0.88 (t, 3H, J = 7.0 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 134.0, 122.9, 81.0, 34.1, 31.8, 29.5, 29.4, 29.3, 29.2, 27.4, 22.6, 20.2, 14.1 ppm; IR (thin film) ν 3368, 3292, 2925, 2854, 1559, 1357, 1182, 930 cm^{-1} .

Characterization data for bicyclic aziridine products from Table 2:

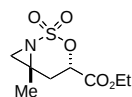
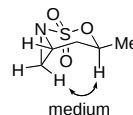


Purified by chromatography on silica gel (1:1 hexanes/EtOAc); white solid (4:1 ds, 84%). **major diastereomer:** TLC R_f = 0.28 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 5.07 (dq, 1H, J = 11.0, 6.5, 4.5 Hz), 3.19 (dddd, 1H, J = 5.0, 3.2 Hz), 2.57 (dd, 1H, J = 5.4, 0.6 Hz), 2.43-2.40 (m, 1H), 2.30 (ddd, 1H, J = 14.4, 8.2, 4.6 Hz), 1.93 (ddd, 1H, J = 14.4, 10.8, 3.2 Hz), 1.42 (d, 3H, J = 6.4 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 79.6, 40.8, 35.8, 26.3, 21.3 ppm; IR (thin film) ν 2988, 2931, 1366, 1187, 971, 863, 798 cm^{-1} ; HRMS (EI) calcd for $\text{C}_5\text{H}_9\text{NO}_3\text{S}$ 163.0303 found 181.0653 (MNH_4^+). **minor diastereomer:** TLC R_f = 0.21 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.59 (dq, 1H, J = 11.4, 6.2, 4.3 Hz), 3.13 (dddd, 1H, J = 5.2, 1.5 Hz), 2.86 (dd, 1H, J = 5.0, 1.8 Hz), 2.61 (ddd, 1H, J = 5.4, 2.0, 0.6 Hz), 2.43 (ddd, 1H, J = 15.4, 11.4, 4.0 Hz), 2.29 (ddd, 1H, J = 15.4, 4.2, 1.6 Hz), 1.46 (d, 3H, J = 6.0 Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 76.2, 40.9, 32.8, 26.1, 21.4 ppm; IR (thin film) ν 2923, 2851, 1361, 1184, 1023, 870, 800 cm^{-1} .

^1H NMR (CDCl_3 , 600 MHz) NOESY correlations for major diastereomer:

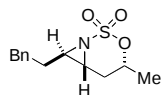


minor diastereomer:



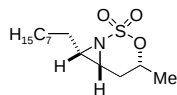
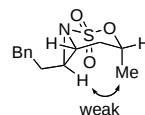
Purified by chromatography on silica gel (7:3 hexanes/EtOAc); white solid (4:1 ds, 92%). **major diastereomer:** TLC R_f = 0.46 (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 5.14 (t, 1H, J = 7.4 Hz), 4.26 (q, 2H, J = 7.1

Hz), 2.76 (s, 1H), 2.48 (dd, 1H, $J = 15.0, 7.0$ Hz), 2.41 (dd, 1H, $J = 15.1, 8.0$ Hz), 2.38 (s, 1H), 1.47 (s, 3H), 1.29 (t, 3H, $J = 7.1$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.8, 76.0, 62.7, 48.2, 41.3, 25.9, 25.2, 14.0 ppm; IR (thin film) ν 2985, 1755, 1446, 1379, 1302, 1191, 1085, 1026, 946, 892, 830 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{13}\text{NO}_5\text{S}$ 235.0514 found 235.0546 (M^+). **minor diastereomer:** TLC $R_f = 0.29$ (1:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 4.84 (dd, 1H, $J = 10.8, 6.4$ Hz), 4.28 (q, 2H, $J = 7.1$ Hz), 2.95 (d, 1H, $J = 2.1$ Hz), 2.65-2.48 (m, 3H), 1.46 (s, 3H), 1.29 (t, 3H, $J = 7.2$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 166.6, 74.2, 62.6, 47.6, 39.2, 26.2, 24.4, 14.0 ppm; IR (thin film) ν 2985, 1758, 1371, 1306, 1185, 1076, 1029, 890, 784 cm^{-1} ; HRMS (EI) calcd for $\text{C}_8\text{H}_{13}\text{NO}_5\text{S}$ 235.0514 found 235.0518 (M^+).



Purified by chromatography on silica gel (7:3 hexanes/EtOAc); colorless oil (2.5:1 ds, 88%). **major diastereomer:** TLC $R_f = 0.28$ (7:3 hexanes/EtOAc); ^1H NMR (CDCl_3 , 500 MHz) δ 7.32-7.28 (m, 2H), 7.23-7.19 (m, 3H), 4.99 (dq, 1H, $J = 11.3, 6.2, 4.3$ Hz), 2.92-2.83 (m, 2H), 2.75 (dt, 1H, $J = 14.0, 8.3$ Hz), 2.59 (dt, 1H, $J = 7.2, 4.9$ Hz), 2.15 (ddd, 1H, $J = 14.5, 8.3, 4.2$ Hz), 1.93-1.85 (m, 3H), 1.37 (d, 3H, $J = 6.5$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.5, 128.5, 128.4, 126.2, 79.5, 48.0, 47.4, 33.3, 32.4, 26.5, 21.2 ppm; IR (thin film) ν 3027, 2933, 1736, 1453, 1375, 1187, 1138, 872, 798 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_3\text{S}$ 267.0929 found 268.1011 (MH^+).

^1H NMR (CDCl_3 , 600 MHz) NOESY correlations for major diastereomer:



Purified by chromatography on silica gel (4:1 hexanes/EtOAc); colorless oil (10:1 ds, 84%): TLC $R_f = 0.23$ (4:1 hexanes/EtOAc); ^1H NMR (CDCl_3 , 400 MHz) δ 5.01 (dq, 1H, $J = 12.0, 6.2, 3.0$ Hz), 3.30 (dt, 1H, $J = 8.9, 5.0$ Hz), 2.69 (dt, 1H, $J = 8.4, 5.4$ Hz), 2.19 (ddd, 1H, $J = 14.4, 8.8, 3.2$ Hz), 2.10-2.01 (m, 1H), 1.71-1.48 (m, 3H), 1.43 (d, 3H, $J = 6.4$ Hz), 1.42-1.20 (m, 11H), 0.88 (t, 3H, $J = 7.0$ Hz) ppm; ^{13}C NMR (CDCl_3 , 100 MHz) δ 79.5, 45.7, 42.5, 31.8, 29.4, 29.3, 29.1, 26.7, 23.9, 23.3, 22.6, 20.9, 14.0 ppm; IR (thin film) ν 2926, 2855, 1458, 1376, 1183, 1134, 875, 797 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{25}\text{NO}_3\text{S}$ 275.1555 found 276.1626 (MH^+).

^1H NMR (CDCl_3 , 600 MHz) NOESY correlations for major diastereomer:

